

Ad- and desorption of Rb atoms on a gold nanofilm measured by surface plasmon polaritons

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Abstract. Hybrid quantum systems made of cold atoms near nanostructured surfaces are expected to open up new opportunities for the construction of quantum sensors and for quantum information. For the design of such tailored quantum systems the interaction of alkali atoms with dielectric and metallic surfaces is crucial and required to be understood in detail. Here, we present real-time measurements of the adsorption and desorption of Rubidium atoms on gold nanofilms. Surface plasmon polaritons (SPP) are excited at the gold surface and detected in a phase sensitive way. From the temporal change of the SPP phase the Rubidium coverage of the gold film is deduced with a sensitivity of better than 0.3% of a monolayer. By comparing the experimental data with a Langmuir type adsorption model we obtain the thermal desorption rate and the sticking probability. In addition, also laser-induced desorption is observed and quantified.

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1. Introduction

Surface plasmon polaritons have been used for a long time as sensitive detectors e.g. for biomolecules. This is mainly done in the so-called Kretschmann configuration by internal reflection of a laser beam from a surface that is coated with a thin metal film [2]. Particles that are close to or stick to the metal film can be detected via their optical properties which shift the surface plasmon angle α_{pl} under which a SPP can be excited. In principle, such shifts can be detected very sensitively by measuring the phase of the reflected light beam which, at the plasmon angle, changes dramatically. However, the fact that the reflectivity is zero at the plasmon angle, i.e the power of the laser beam is completely transferred into a plasmonic excitation, broadens the detectable phase shift and limits the sensitivity [3]. Recently, a new excitation scheme has been introduced which avoids this problem by an electronic feedback on the phase of the incident laser field [1]. In the work presented here, this scheme is used for the first time to actually measure the optical properties of a sample. The work is mainly motivated by recent progress in the field of surface quantum optics, atom chips and hybrid quantum systems. Such tailored quantum systems made of cold atoms near nanostructured surfaces are expected to open up new opportunities for the construction of quantum sensors and for quantum information. In this context, we recently studied clouds of ultracold atoms coupled to evanescent waves near solid surfaces [4]. The enhancement of such optical near-fields by the excitation of surface plasmons is already known for some time [5], but only recently, proposals have been put forward to generate plasmonic nanopotentials for the manipulation and trapping of cold atoms [6, 7]. For the design of such traps, surface potentials such as Casimir-Polder potentials [8] have to be taken into account and some effort has been invested by the cold atoms community for studying dissipative forces [9, 10, 11, 12, 13]. However, additional potentials from particles adsorbed at the surface are only little considered. As has been shown experimentally [14], such potentials can dramatically influence atom traps near surfaces. Thus it is crucial to understand and control atomic adsorption, e.g. by laser-induced atomic desorption (LIAD) [15]. Furthermore, fascinating ideas have been proposed that rely on the controlled adsorption of atoms on semiconductor surfaces, which might prove as an important technological step towards the manipulation of electronic nano devices [16].

Here, we report on adsorption of thermal Rubidium atoms on a gold nanofilm. The Rubidium coverage is monitored by the phase shift in the excitation spectrum of surface plasmon polaritons. By rapidly changing the Rubidium vapor pressure, the balance between adsorption and thermally induced desorption is perturbed and reequilibration is monitored in real time. The observations are compared to a simple Langmuir type model and the parameters of the model are extracted from the data.

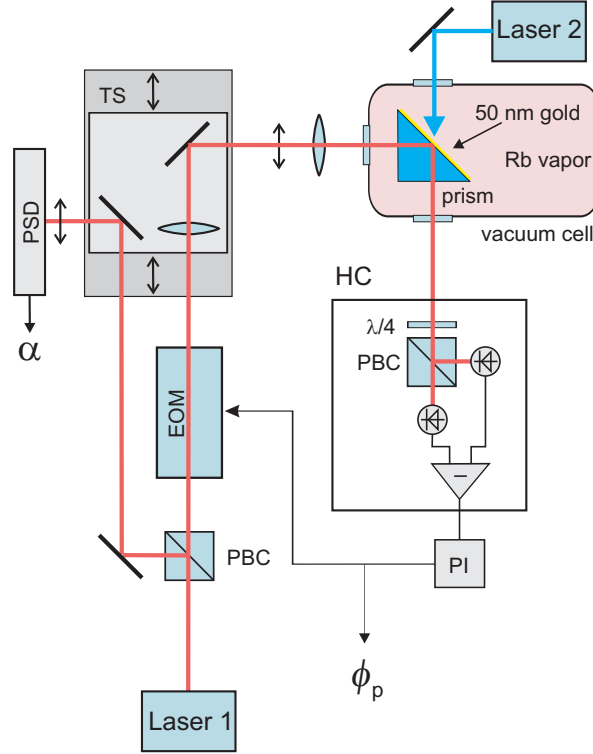


Figure 1. Experimental setup. Laser 1 excites plasmons at the surface of a gold coated prism inside a vacuum chamber with a variable Rubidium (Rb) vapor pressure. The angle α at which the laser beam hits the surface is varied with a translation stage (TS). It shifts the beam relative to the lens which guides the beam to the prism surface. The position of the translation stage is monitored with an auxiliary laser beam and a position-sensitive diode (PSD). The beam reflected from the surface is analyzed by a Hänsch-Couillaud (HC) setup. It consists of a $\lambda/4$ retardation plate, a polarizing beam splitter cube (PBC) and a pair of differential photodiodes. The recorded signal is controlled by a PI feedback loop which acts on the phase of the incident light field via an electro-optic modulator (EOM). The feedback-voltage is directly proportional to the phase of the reflected light field ϕ_p . For laser-assisted desorption of atoms the gold surface can be exposed to a second laser beam (laser 2).

2. Experimental setup

The ad- and desorption of Rubidium atoms is observed by phase sensitive detection of the surface plasmon resonance. The experimental setup is shown in figure 1. The beam from a grating stabilized diode laser (laser 1, wavelength near the D2-line of ^{87}Rb at $\lambda = 780$ nm, laser power $P = 10$ mW, laser bandwidth 2 MHz) is internally reflected from the gold-coated surface of a dielectric prism. The incident angle α at which the laser hits the prism surface can be adjusted with a mirror mounted onto a mechanically driven translation stage (TS). It shifts the beam relative to a lens which guides the beam to the prism surface. The position of the translation stage is monitored with an auxiliary laser beam and a position-sensitive diode (PSD). The guiding lens is the second lens in a $2f$ telescope with the first lens being attached to the translation stage. By

that the incident beam is collimated at the prism surface. At a characteristic plasmon angle $\alpha = \alpha_{\text{pl}}$ surface plasmons are excited by the p-polarized fraction of the incoming light. The incident light is absorbed by the plasmon excitation and the reflectivity for p-polarized light r_p drops to a minimum (figure 2). If Rubidium atoms are adsorbed, the value of the plasmon angle shifts and the phase of the p-polarized fraction of the reflected light field ϕ_p changes. This phase change is monitored with a standard Hänsch Couillaud (HC) setup [19]. A PI-servo electronics feeds the signal to an electro-optic modulator (EOM) that controls the phase of the incident laser light [1]. This locks the Hänsch Couillaud signal to zero such that the control-voltage at the EOM is directly proportional to ϕ_p .

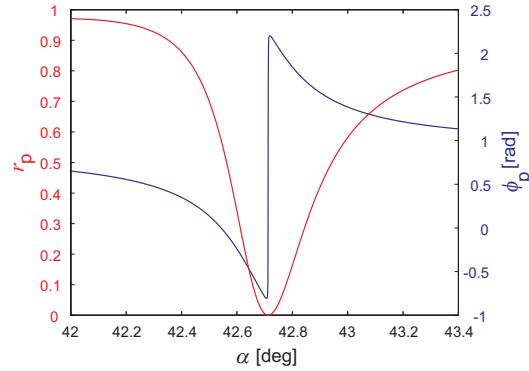


Figure 2. Theoretical reflection coefficient r_p and phase shift ϕ_p of the reflected p-polarized light field. The incidence angle α is varied around the surface plasmon angle at 42.7° .

The gold film on the prism surface has been fabricated by e-beam evaporation and has a thickness of approximately 50 nm. Below the gold film a very thin layer of titanium has been added for improving adhesion of the gold to the glass substrate. The prism is placed inside a vacuum chamber at a base pressure of $5 \cdot 10^{-9}$ mbar and is mounted to a temperature controlled heating. The partial pressure of Rb in the chamber is controlled by a resistively heated dispenser and can be raised within a few seconds up to several 10^{-6} mbar. Laser induced desorption of Rb atoms can be investigated with an additional blue laser beam at a wavelength near 406 nm and a maximum power of 20 mW (laser 2)[20].

3. Theoretical model

The interpretation of our experiment is based on the observation that, according to Brunauer, Emmet and Teller (BET), only fractions of a monolayer can be adsorbed if the vapor pressure of an adsorbant is smaller than the saturation vapor pressure $p < p_{\text{sat}}$ [17]. Thus the surface coverage Θ only takes values between 0 and 1, i.e. $0 < \Theta < 1$.

We model the temporal change of the surface coverage by the rate equation

$$\dot{\Theta} = -C\Theta + I_{\text{in}}\sigma S(\Theta), \quad (1)$$

with a desorption constant C , an impinging flux of atoms on the surface I_{in} , a typical area per adsorbed atom of $\sigma = 10^{-15} \text{ cm}^2$ and a sticking probability $S(\Theta)$. The atomic flux hitting the surface is given by $I_{\text{in}} = nv/4$ with the factor 4 following from integrating the Knudsen cosine law over a half sphere, the ideal gas vapor density $n = p/k_B T$ and the thermal velocity of the atoms $v = (2k_B T/m)^{1/2}$. For simplicity we define the flux per pressure R in units of adsorbed monolayers via $I_{\text{in}}\sigma \equiv Rp$, i.e. $R = \sigma(1/8mk_B T)^{1/2}$. The sticking probability is taken from the Langmuir model $S(\Theta) = S_0 \cdot (1 - \Theta)$, with the initial sticking probability S_0 [18]. Note that $S(\Theta)$ vanishes for full coverage ($\Theta = 1$). This guaranties that only fractions of a monolayer can be adsorbed. With these definitions (1) reads

$$\dot{\Theta} = -(C + S_0 Rp)\Theta + S_0 Rp, \quad (2)$$

In equilibrium ($\dot{\Theta} = 0$) the surface coverage is given by

$$\Theta_{\text{eq}} = \frac{1}{1 + C/S_0 Rp}. \quad (3)$$

The equilibrium coverage depends on the pressure in the chamber. If the pressure is rapidly changed the new equilibrium is exponentially reached within an $1/e$ -timescale

$$\tau = \frac{1}{C + S_0 Rp}, \quad (4)$$

as can be deduced from (2).

4. Observations

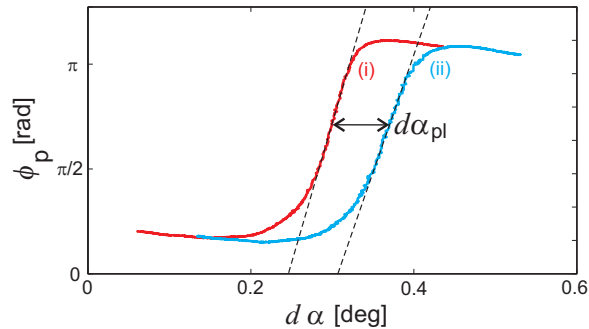


Figure 3. Phase ϕ_p vs. incidence angle shift $d\alpha$ before (i) and after (ii) adsorption of Rb atoms.

We measure the adsorption of rubidium with the above mentioned setup by two different methods. In the first method the incidence angle is scanned and from the obtained signal the position of the plasmon angle is determined. This method is applicable for a plasmon angle which changes only little during the scan time of approximately one

minute. Figure 3 shows an example. The relation between the shift of the plasmon angle $d\alpha_{\text{pl}}$ and the thickness of the adsorbed layer dl is taken from a four-layer matrix model (layer 1: glass substrate, layer 2: gold film, layer 3: Rb adsorbate, layer 4: vacuum) which takes multiple reflections at the boundaries into account [21]. With the dielectric constant of gold $\epsilon_{\text{Au}} = -22.9 + 1.42 \times i$ and Rb $\epsilon_{\text{Rb}} = -4 + 0.42 \times i$ [22, 23] the result is $d\alpha_{\text{pl}}/dl = 0.1^\circ/\text{nm}$. The observed shift of the plasmon angle in figure 3 of $d\alpha_{\text{pl}} = 0.072^\circ$ thus corresponds to an adsorbed Rb layer thickness of $l = 0.72 \text{ nm}$.

The second, more sensitive method records the phase ϕ_p with the incidence angle held fixed at the plasmon angle. Adsorption and desorption of atoms can now be observed in real time by looking at the temporal change of the phase ϕ_p . For not too large variations of α_{pl} the relation between plasmon angle and phase is linear with a slope of $d\phi_p/d\alpha_{\text{pl}} = 42.1 \text{ rad}/^\circ$ that is taken from the left curve in figure 3. Note that after adsorption of Rb (right curve) the slope is with $d\phi_p/d\alpha_{\text{pl}} = 35.1 \text{ rad}/^\circ$ slightly smaller. For large changes of the plasmon angle the working point is shifted from the linear regime to a regime where the phase change saturates. Thus the second method can only be applied for small changes of the plasmon angle, unless the incidence angle is recalibrated. Typical data are shown in figure 4. In (a) the Rb vapor pressure is quickly increased by activating the dispenser for about 80s (curve (ii)). The pressure is determined with a standard ion-gauge. Curve (i) shows the resulting change of the phase Φ_p . During the pulsed increase of the vapor pressure the Rubidium coverage also grows and remains at an increased value after the puls. Figure 4 (b) shows a similar measurement with higher resolution which allows to estimate the sensitivity of the method. After low pass filtering the signal with an integration time of $T = 50 \text{ ms}$ the noise of the phase signal is on the order of $\Delta\phi_p = 5 \times 10^{-3} \text{ rad}$. At this noise level the uncertainty of the measured layer thickness is $\Delta l = \Delta\phi_p \cdot d\alpha_{\text{pl}}/d\phi_p \cdot dl/d\alpha_{\text{pl}} = 1.2 \text{ pm}$. With an average distance between two atoms given by twice the covalent radius of Rb of $2r_c = 440 \text{ pm}$, the sensitivity amounts to better than $\Delta l/2r_c = 0.3\%$ of an adsorbed monolayer. This sensitivity corresponds to a resolveable relative refractive index change of $\Delta n/n = 2 \cdot 10^{-6}$.

In the experiment the gold surface is heated to a temperature of $T_S = 68^\circ \text{ C}$. The resulting Rb saturation vapor pressure of $p_{\text{sat}} = 2 \cdot 10^{-5} \text{ mbar}$ is one order of magnitude larger than the maximum Rb vapor pressure in the experiment of $p_{\text{max}} = 2 \cdot 10^{-6} \text{ mbar}$. The above assumption of a fractional coverage is thus well justified. In figure 5 the observed coverage Θ is plotted during and after a temporal increase of the Rb vapor pressure. During the first 20 min the pressure stays very much near a value of about $p = 1 \cdot 10^{-7} \text{ mbar}$. The coverage growth rate at this pressure can be derived by linearly extrapolating the coverage increase with time. We obtain $d\Theta/dt = (150 \text{ min})^{-1}$. Putting this value into (2) and setting $\Theta = 0$ the initial sticking coefficient can be determined to be $S_0 = 0.8\%$. After 200 min we reduce the pressure back to a value of $p = 7 \cdot 10^{-8} \text{ mbar}$. Now the atoms thermally desorb and the coverage decays exponentially. The thermal desorption constant $C = C_{\text{th}}$ can be determined from (4) by measuring the $1/e$ decay

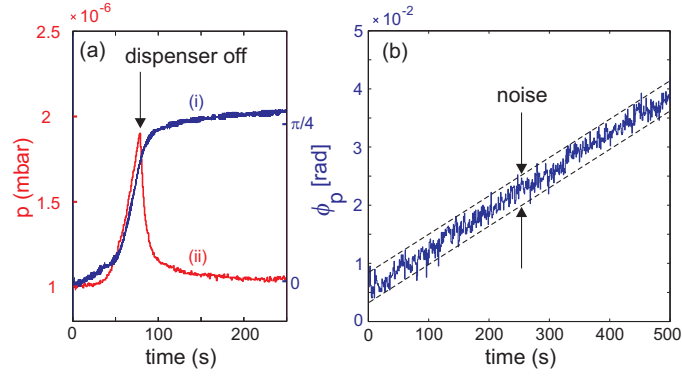


Figure 4. (a) Observed phase shift (i) and Rb vapor pressure (ii) after activating the Rb dispenser at time = 0 for a period of 80s. (b) Estimation of the experimental phase noise level.

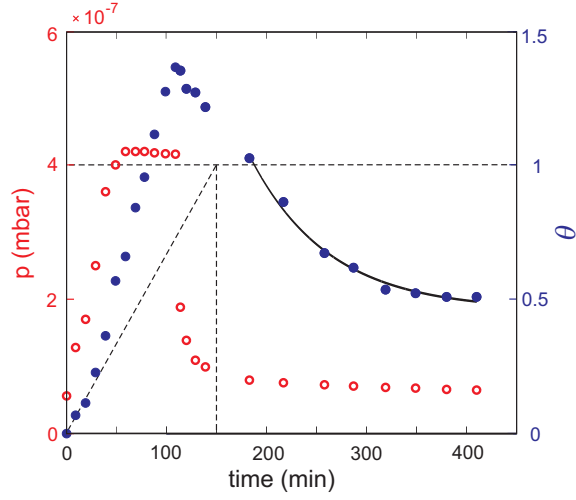


Figure 5. Observed monolayer coverage (blue solid dots, right vertical axis) during and after a temporal increase of the Rb vapour pressure (red open circles, left vertical axis). From the linear coverage growth during the first 20 minutes (black dotted line) the growth time per monolayer can be deduced. The decay of the coverage after the pulse is fitted with an exponential function.

time τ . Fitting an exponential curve to the data yields $\tau = 4.7 \cdot 10^3$ s. For the desorption constant we obtain $C = 1/\tau - S_0 R p = 1.3 \cdot 10^{-4} \text{ s}^{-1}$. In order to show the consistency of the model with the determined parameters the equilibrium coverage is calculated from (3) to be $\Theta_{\text{eq}} = 0.4$. This value is comparable to the observed value in figure 5 of $\Theta_{\text{eq}} = 0.5$.

The equilibrium coverage can be further reduced by exposing the surface to a laser beam with a wavelength near 406 nm (20 mW laserpower, beam diameter 1 mm). Figure 6 shows the resulting change of the surface coverage $d\Theta$. As soon as the blue laser is turned on, the coverage decreases in time with a rate of $\dot{\Theta} = -4.4 \cdot 10^{-5} \text{ s}^{-1}$. The total desorption coefficient is now the sum of the thermal and the laser-induced desorption coefficient $C = C_{\text{th}} + C_{\text{li}}$. With (2) and for $\Theta = 0.5$ and a pressure of $p = 2 \cdot 10^{-7}$ mbar

the total desorption coefficient amounts to $C = 3.1 \cdot 10^{-4} \text{ s}^{-1}$. This results in a pure laser-induced desorption rate of $C_{\text{li}} = 1.8 \cdot 10^{-4} \text{ s}^{-1}$ at a laser power of 20 mW. The new equilibrium coverage of $\Theta_{\text{eq}} = 0.42$ is reached within a $1/e$ time of $\tau = 1.9 \cdot 10^3 \text{ s}$.

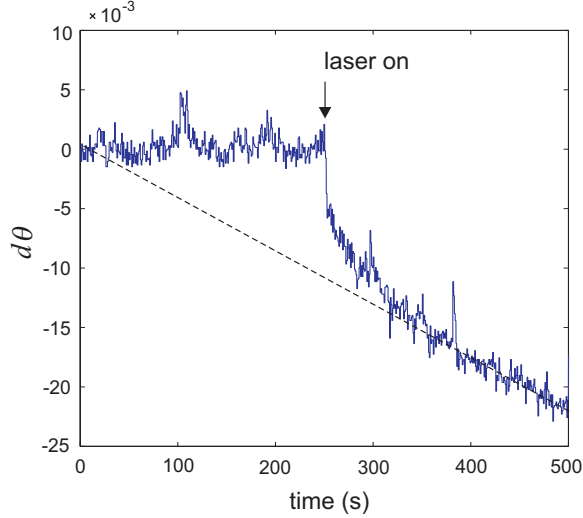


Figure 6. Laser-induced desorption of Rb. If the surface is exposed to blue laser light, the surface coverage starts to decrease.

5. Conclusion

We have applied a recently introduced method [1] for detecting de- and adsorption phenomena by means of phase-sensitive detection of a surface plasmon resonance to Rubidium on a gold surface. Adsorption and desorption of Rb were observed and interpreted with a rate model. We reach a sensitivity of better than 0.3% of a monolayer, respectively a refractive index unit change of $\Delta n = 2 \cdot 10^{-6}$ RIU within an integration time of 50 ms. This is comparable to typical sensitivities reached with surface plasmon resonance sensors [24]. The observed sensitivity in this paper is limited by technical noise which leaves much room for substantial improvement, e.g. by a shot-noise limited detection scheme, by suppression of laser frequency noise, and by longer integration time. As has been shown in [1], a resolution of $\Delta n = 2 \cdot 10^{-8}$ RIU within an integration time of 0.1 s seems feasible even far above the shot-noise limit. Such a sensitivity exceeds the best values reported for conventional detectors, e.g. in [25]. By comparing the experimental data with a Langmuir type adsorption model we find a desorption constant of $C = 1.3 \cdot 10^{-4} \text{ s}^{-1}$ and an initial sticking probability $S_0 = 0.8\%$. Laser-assisted desorption has been observed. A desorption coefficient of $C_{\text{li}} = 1.8 \cdot 10^{-4} \text{ s}^{-1}$ is determined for a laser power of 20 mW.

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References

- [1] König T, Weidemüller M and Hemmerich A 2008 *Appl. Phys. B* **93** 545
- [2] Kretschmann E and Raether H 1968 *Z. Naturforsch.* **28a** 2135
- [3] Ran B and Lipson S G 2006 *Opt. Express* **14** 5641
- [4] Bender H, Courteille P, Zimmermann C and Slama S 2009 *Appl. Phys. B* **96** 275
- [5] Esslinger T, Weidemüller M, Hemmerich A and Hänsch T W 1993 *Opt. Lett.* **18** 450
- [6] Chang D E, Thompson J D, Park H, Vuletic V, Zibrov A S, Zoller P and Lukin M D 2009 *Phys. Rev. Lett.* **103** 123004
- [7] Murphy B and Hau L V 2009 *Phys. Rev. Lett.* **102** 033003
- [8] Casimir H B G and Polder D 1948 *Phys. Rev.* **73** 360
- [9] Sandoghdar V, Sukenik C I, Hinds E A and Haroche S 1992 *Phys. Rev. Lett.* **68** 3432
- [10] Sukenik C I, Boshier M G, Cho D, Sandoghdar V and Hinds E A 1993 *Phys. Rev. Lett.* **70** 560
- [11] Grisenti R E, Schöllkopf W, Toennies J P, Hegerfeldt G C and Köhler T 1999 *Phys. Rev. Lett.* **83** 1755
- [12] Obrecht J M, Wild R J, Antezza M, Pitaevskii L P, Stringari S and Cornell E A 2007 *Phys. Rev. Lett.* **98** 063201
- [13] Bender H, Courteille Ph W, Marzok C, Zimmermann C and Slama S 2010 *Phys. Rev. Lett.* **104** 083201
- [14] McGuirk J M, Harber D M, Obrecht J M and Cornell E A 2004 *Phys. Rev. A* **69** 062905
- [15] Meucci M, Mariotti E, Bicchi P, Marinelli C and Moi L 1994 *Europhys. Lett.* **25** 639
- [16] Judd T E, Scott R G, Sinuco G, Montgomery T W A, Martin A M, Krüger P and Fromhold T M 2010 *NJP*, to be published, arXiv:0912.1846
- [17] Brunauer S, Emmett P H and Teller E 1938 *J. Am. Chem. Soc.* **60** 309
- [18] Masel R I 1996, *Principles of Adsorption and Reaction on Solid Surfaces* John Wiley and Sons (New York)
- [19] Hänsch T W and Couillaud B 1980 *Opt. Commun.* **35** 441
- [20] Klempt C, van Zoest T, Henninger T, Topic O, Rasel E, Ertmer W and Arlt J 2006 *Phys. Rev. A* **73** 013410
- [21] Deutsch I H, Spreeuw R J C, Rolston S L and Phillips W D 1995 *Phys. Rev. A* **52** 1394
- [22] Etchegoin P G, Le Ru E C and Meyer M 2006 *J. Chem. Phys.* **125** 164705
- [23] Smith N V 1970 *Phys. Rev. B* **2** 2840
- [24] Homola J, Yee S S, Gauglitz G 1999 *Sens. and Act. B* **54** 3
- [25] Kabashin A V, Patskovsky S and Grigorenko A N 2009 *Opt. Express* **17** 21191